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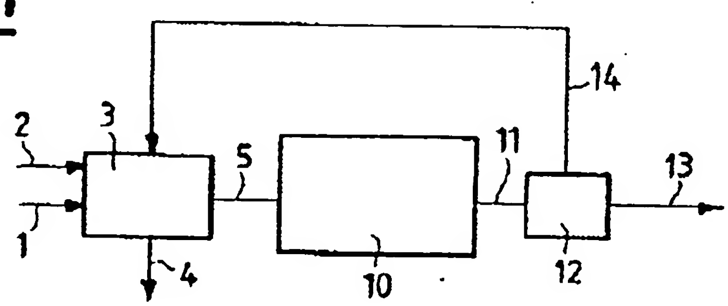
(54) **Process of catalytic partial oxidation of natural gas in order to obtain synthesis gas and formaldehyde.**

(57) Process of catalytic partial oxidation of natural gas in order to obtain synthesis gas and formaldehyde, integrated with processes of hydrogenation of the resulting CO, such as Fischer-Tropsch and methanol syntheses. Such an oxidation is carried out by means of a catalyst constituted by one or more compounds of metals form Platinum Group, which is given the shape of wire meshes, or is deposited on a carrier made from inorganic compounds, in such a way that the level of metal or metals from Platinum Group, as percent by weight, is comprised within the range of from 0.1 to 20% of the total weight of catalyst and carrier, by operating at temperatures comprised within the range of from 300 to 950 °C, under pressures comprised within the range of from 0.5 to 50 Atm, at space velocities comprised within the range of from 20,000 to 1,500,000 h^{-1}.

Fig.1



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The present invention relates to a catalytic partial oxidation process (which in the present patent application will be referred to, briefly, as "CPO") of natural gas in order to obtain synthesis gas and formaldehyde; more particularly, it relates to the production of synthesis gas for Fischer-Tropsch (F-T) processes, to processes for methanol and methanoldimethylether mixtures synthesis under conditions of high conversion rate per pass.

The synthesis gas is presently manufactured by means of processes of steam reforming, autothermal reforming, non-catalytic partial oxidation of hydrocarbons. The steam reforming processes catalytically convert mixtures of hydrocarbons and steam (H_2O/C = 2.5-3.5 by vol/vol) into mixtures of CO and H_2 with a H_2/CO ratio typically of round 3 when the process is carried out by starting from natural gas. The main reactions which describe the process are

$C_nH_m + nH_2O \longrightarrow nCO + (m+n/2)H_2$ [1]

$H_2O + CO \longrightarrow CO_2 + H_2$ [2]

The H_2O:C ratio in the reactant mixture is determined by the temperature and pressure conditions under which the reactions are carried out, as well as by the need for inhibiting the coal formation reactions [3] and [4]:

$C_nH_m \longrightarrow C_n + m/2\ H_2$ [3]

$2CO \longrightarrow C + CO_2$ [4]

The commonly used catalysts in this process are based on Ni supported on Al, Mg, Si oxide carriers. The used carriers display high thermal stability and mechanical strength characteristics. The reactions take place inside tubular reactors contained inside a combustion chamber. The pressures inside the tubes are typically comprised within the range of from 1 to 5 MPa, and the temperature at tube outlets is typically higher than 850°C (see, e.g., Catalysis Science and Technology" Vol. 5, Chapter 1, J.R. Rostrup-Nielsen). The stay times of the gas streams inside the interior of the catalytic beds are of round five seconds. A long the reforming tubes (which are approximately 15-m long), which are totally filled with catalyst, large gradients arise in the gas mixture composition.

The processes of non-catalytic partial oxidation are less widely used and are employed in order to convert mixtures of hydrocarbons, oxygen, steam and air into synthesis gas with H_2/CO ratios of typically round 2 if one starts from natural gas. The process chemistry can be represented by means of equations [5] and [2]

$C_nH_m + n/2\ O_2 \longrightarrow nCO + m/2\ H_2$ [5]

The facilities installed to date by Texaco and Shell (see Hydrocarbon Processing; April 1990, p. 99) are provided with adiabatic reactors in which the reactions are started inside the reactors by means of a burner in which the reactions of total combustion [6] of hydrocarbons

$C_nH_m + (n+m/2)O_2 \longrightarrow n\ CO_2 + m/2\ H_2O$ [6]

mainly take place.

These reactions produce large amounts of heat, steam and CO_2. Heat causes cracking reactions of unburnt hydrocarbons to take place, and favours the reaction of steam- and CO_2-reforming [1], [7]

$nCO_2 + C_nH_m \longrightarrow 2nCO + m/2\ H_2$ [7]

The process temperatures are typically comprised within the range of from 1250 to 1500°C and pressure is caused to range from 3 to 12 MPa. The process requires very short stay times of the reactant/product mixture inside the reactor (of about 0.5 seconds). As in the reactant mixtures ratios of $O_2:CH_4$ are used which are normally larger than 0.6 (by vol/vol), the produced syn gas contains large amounts of CO_2.

The autothermal reforming processes are carried out insid adiabatic r actors to which mixtures of hydrocarbons, oxygen and steam are fed: also in this case, the $O_2:CH_4$ ratios are larger than the stoichiom tric value of 0.5. In a first reaction zone, by means of a burner the total combustion reactions of

hydrocarbons [6] ar started. in a second reaction zone, inside a catalytic bed the steam [1] and CO_2 reforming [7] reactions take place. In the catalytic bed, catalysts are used which display similar characteristics to those as described above for steam reforming processes. From autothermal reforming, synthesis gas mixtures are obtained with intermediate H_2:CO ratios between those found in syn gas from steam reforming and non-catalytic partial oxidation, respectively. The reactor outlet temperature is typically comprised within the range of from 900 to 1000 °C, but the temperature inside the zone in which the burner is installed is considerably higher. The internal reactor pressure is comprised within the range of from 2 to 4 MPa. The stay times inside the catalytic bed are of round 0.7 seconds.

Synthesis gas is mainly used in F-T syntheses in order to obtain hydrocarbon blends, in methanol synthesis, in ammonia synthesis.

F-T processes have been mainly realized by Sasol in South Africa and use synthesis gas produced from coal by means of a coal gasification and methane reforming process. The investment costs for the Sasol facilities are subdivided as follows (see M.E. Dry "The Fischer-Tropsch synthesis -- Commercial aspects" Catal. Today, 1990, 6, 183):

-- coal mining, steam and O_2 production	47%
-- synthesis gas production	23%
-- F-T synthesis	30%

As one may see, the coal mining and conversion costs and the syn gas production costs constitute approximately 70% of total process costs and producing fuels from coal is economically feasible if one has available coal at much lower costs than of petroleum. The syn gas mixtures obtained from Sasol process contain H_2:CO ratios comprised within the range of from 1.7 to 2.

F-T synthesis mainly produce hydrocarbons according to equation [8]

$$2nH_2 + nCO \dashrightarrow C_nH_{2n} + nH_2O \qquad [8]$$

In reality, F-T synthesis is a process of polymerization of C_1 units in which saturated and unsaturated, straight and branched-chain hydrocarbons are produced.

In general, the presently available technologies of hydrogenation of carbon monoxide downstream from the steam reforming, autothermal reforming, partial oxidation processes require that methane levels are lower than 5%. The reactions of hydrogentaion of carbon monoxide with mixtures of pure CO and H_2 display lower conversion rates than 70%. Low levels of methane in synthesis gas are necessary in order to increase the partial pressures of CO and H_2 and prevent kinetic and thermodynamic constraints from causing the conversion rates, experienced in CO hydrogenation reactions, to decrease. A decrease in conversion rate implies an increase in the amounts of reactants to be recycled and CH_4 accumulating during the recycles.

Owing to these reasons, the target is values of methane conversion rate higher than 95%. Since 1985, processes for the synthesis of diesel fuels from natural gas have been developed, which are based on an intermediate syn gas production, a F-T synthesis of long-chain hydrocarbons, and a hydrocracking of the latter. In this case too, the step of syn gas production contributes for approximately 60% to total production costs.

Also in conventional methanol production processes, at temperatures comprised within the range of from 220 to 300 °C, the syn gas production costs contribute with similar percent amounts.

Therefore, in F-T syntheses and in methanol syntheses by means of the conventional routes, synthesis gas mixtures are use which contain negligible levels of methane in order to prevent that a decrease in H_2 and CO partial pressure may cause both a decrease in reaction rates and consequendy in conversion rates per pass, and methane accumulating in the recycled gas to the synthesis step.

On the contrary, the methanol syntheses with high conversion rates per passage, operating at low temperatures, are capable of converting approximately 90% of synthesis gas into methanol even in the presence of large amounts of inert gases. However, in this case, CO_2 and H_2O impurities are not tolerated in the reactant mixtures.

This process was mainly studied by Shell (EP-285 228; EP-287 151; EP-289 067; EP-306 113; EP-306 114; EP-309 047; EP-317 035), Brookhaven National Laboratories (US-4 935 395; US-4 614 749; US-4 623 634; US-4 613 623), Mitsui (JP-81/169 934; JP-82/128 642), Sintef (WO-86/3190), Snamprogetti (IT 20.028 A/88; IT 23,101 A/88; IT 23,102 A/88; IT 22.352 A/89; EP 357 071, EP-504 981).

The catalytic systems which are used in these syntheses contain nickel [Ni(CO)$_4$/MeONa] or copper (CuCl/MeONa, copper chromite/MeONa) and the syntheses are carried out in slurry reactors. The reactions take place at temperatures comprised within the range of from 90 to 120 °C and the pressures are comprised within the range of from 5 to 50 atm. Under these conditions, conversion rates of round 90% and selectivities higher than 95% are obtained by using CO and H_2 mixtures (with H_2:CO ratios = 2 by vol/vol) and high levels of such inert molecules as nitrogen and methane (typically, reactions were studied in which the inerts levels were of approximately 40%).

Also the syntheses of methanol-dimethyl ether mixtures can be carried out with high values of conversion per pass, because the formation of dimethyl ether with consequent methanol shift favours the obtainment of total conversions of CO/H_2 mixture [J. Bogild Hansen, F. Joensen – Stud. Surf. Sc. Catal., 61 (1991), 457]. Therefore, also in this case, the reaction can be carried out in the presence of such an inert gas as non-converted methanol.

It has now been found a process of catalytic partial oxidation (CPO) of natural gas to yield synthesis gas, using a noble metal containing catalyst, carried out at ultra high space velocity (UHSV), at considerably lower temperatures than as presently used and with even particularly low O_2:C and H_2O:CH_4 molar ratios, which process can be strongly integrated with processes of carbon monoxide hydrogenation, such as F-T syntheses and methanol or methanol-dimethyl ether mixtures syntheses.

Formaldehyde is a byproduct from the present process and is separated before using syn gas when formed in relatively large amounts, e.g., in larger amounts than about 3% by weight.

The possibility of operating at higher space velocities (1,500,000 > GHSV > 20,000 h^{-1}) than has presently used (GHSV < 10,000 h^{-1}) makes it possible small size reactors to be used, thus allowing savings to be accomplished in investment costs. The possibility of operating with reactant streams with molar ratios of O_2:CH_4 < 0.5 (by vol/vol), makes it possible the energy consumptions and the investment costs for oxygen production units, to be decreased.

The processes of catalytic partial oxidation of methane [12], carried out at lower space velocities than 15,000 h^{-1}, can be described as the sum of total hydrocarbon combustion [9] and steam and CO2 reforming reactions [10]-[11]

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O \qquad [9]$$

$$CO_2 + CH_4 \longrightarrow 2CO + 2\,H_2 \qquad [10]$$

$$H_2O + CH_4 \longrightarrow CO + 3\,H_2O \qquad [11]$$

$$CH_4 + 1/2\,O_2 \longrightarrow CO + 2\,H_2 \qquad [12]$$

At lower temperatures than 600 °C, the total oxydation reaction [9], strongly exothermic, is considerably favoured, whilst the steam and CO_2 reforming reactions [10]-[11], strongly endothermic, are unfavoured. On the contrary, at higher temperatures than 750 °C, both these latter reactions are capable of converting CO_2 and H_2O into synthesis gas.

The catalysts used in the CPO step according to the present invention makes it possible the reactions to be carried out with O_2:CH_4 ratios lower than 0.5 also in the absence of steam, under conditions which at present can not be used with the catalysts known from the prior art, owing to the coal formation reactions [3] and [4]. The synthesis gas produced under these conditions may contain even large amounts (of up to 50%) of unreacted methane and can be used in synthesis reactions with high conversion rate values per pass.

The influence of the high value of space velocity is reported in published studies by D.A. Hickman and L.D. Schmidt (Science 1993, 259, 343), which made experiments at higher temperatures than 1000 °C with rhodium-based catalysts, and by V.R. Choudari, A.S. Mamman, S.D. Sansare (Angew. Chem. Int. Ed. Engl. 1992, 31, 1189), which performed experimental tests at temperatures comprised within the range of from 300 to 900 °C, with catalysts not constituted by noble metals (Fe, Co, Ni). The experimental tests disclosed in the present patent application are anyway different from those reported in published papers. The above Authors used different catalysts from those we studied, and consequently were unable to operate with O_2:CH_4 ratios < 0.5 (by vol/vol) in order to avoid the coal formation reactions [3], [4] and did not obtain HCHO; furthermore, the CPO process according to the present invention enables synthesis gas to be produced under UHSV conditions even in the pres nce of large amounts of CO_2. The possibility of using CO_2 in the reactant mixture makes it possible considerable advantages to be gained whenever syn gas mixtures with H_2:CO ratios lower than 2 (by vol/vol) must be obtained. Such low values of said ratio are

advantageous for producing long-chain and high-molecular-weight hydrocarbon in F-T syntheses. As we already briefly mentioned, long-chain hydrocarbon products can b converted into diesel fuels for engines for motor vehicles.

At the high space velocity values used in the CPO process according to the present patent application, the selectivity characteristics of CPO reactions are meaningfully changed. Carbon monoxide and hydrogen are produced With extremely high selectivity values even at low temperatures. The catalysts used in the experimental studies on CPO disclosed in the present patent application are considerably different from those reported in technical papers, because they may contain decidedly low levels of noble metal (down to 0.1%).

The syn gas production reactions are thought to be representable as follows:

$$
\begin{tikzcd}
CH_4 + O_2 \arrow[r] \arrow[d] & CO_2 + H_2O \arrow[r, "CH_4"] & CO + H_2 \\
CO + H_2 \arrow[ur] & &
\end{tikzcd}
$$

According to presently current opinions, people think that under high space velocity conditions, the primary products from oxidation reactions CO and H_2 may be obtained, which are then rapidly removed from catalyst surface before reacting to form the secondary reaction products.

The process of catalytic partial oxidation of natural gas in order to obtain synthesis gas and formaldheyde, the first object of the present invention, is characterized in that such an oxidation is carried out by means of a catalyst constituted by one or more compounds of metals from Platinum Group, which are given the shape of wire meshes, or are deposited on a carrier made form inorganic compounds, in such a way that the percent level of metal or metals from Platinum Group, by weight, is comprised within the range of from 0.1 to 20%, preferably of from 0.1 to 5% of the total weight of catalyst and carrier, by operating at temperatures comprised within the range of from 300 to 950 °C, preferably of from 350 to 850 °C, under pressures comprised within the range of from 0.5 to 50 atm, preferably of from 1 to 40 atm, at space velocities comprised within the range of from 20,000 to 1,500,000 h^{-1}, preferably of from 100,000 to 600,000 h^{-1}.

The used catalysts are particularly active as regards the CPO reactions, and are particularly inert as regards the coal formation reactions [3], [4] and are even capable of working with O_2:CH_4 ratios lower than 0.5 (by vol/vol), and in the presence of CO_2 without undergoing deactivation. In those cases when the ratio of O_2:CH_4 is lower than 0.5, in the CPO reactor leaving streams high contents of unreacted methane will be obtained.

If the CPO reactions are carried out by using reactants mixtures with ratios of O_2/CH_4 = 0,65 (by vol-vol), the methane content in leaving streams can be reduced down to levels which may even be lower than 5%.

As already briefly mentioned, CPO catalysts are used which contain metals from Platinum Group, in pellet form, prepared according to procedures disclosed in patent literature (UK Patent No. 2 240 284, UK Publ.No.2247465, IT-MI92A 001953, UK Publ. No. 2274284). Furthermore, in the CPO step, noble metals wire meshes can be used which are similar to those as used in nitric acid production, but with a higher Rh content than 9% by weight, or, still, enbloc catalysts. In particular in the latter case, in the present patent application an original method for preparing enbloc catalysts is disclosed, which makes it possible the noble metals to be rapidly deposited With a high dispersion degree, onto the surface of the monolithic body, by dipping the latter in an organic solution of organometallic Rh, Ru, Ir clusters. The metals get fixed on the surfaces of the monolithic body through a solid-liquid reaction between the reactive surface sites and the organometallic clusters, which then undergo decomposition, until monoatomic species in an extremely highly dispersed state are produced. This procedure is substantially different from the impregnation processes, because the noble metal content which is fixed onto the carrier is determined by the number of active sites present on the surface of the latter.

A further object of the present invention are the integrated processes for methanol or methanol-dimethyl ether syntheses and for F-T syntheses.

The integrat d process for methanol synthesis from synthesis gas essentially consists in causing the synthesis gas obtained by means of the process disclosed hereinabove, after the preliminary possible

separation of formed formaldehyde, to react, by means of a suitable catalyst, by operating, in the case of the high-conversion-per-pass synthesis, after additionally separating CO_2 and H_2O from said synthesis gas, at a temperature which is higher than 40 °C and lower than 200 °C and under a higher pressure than 1 MPa; or, in the case of the syntheses carried out by the conventional route, at a temperature higher than 200 °C and lower than 350 °C, and under a higher pressure than 0.3 MPa.

The integrated process for the synthesis of methanol-dimethyl ether mixtures consists in causing the mixture of synthesis gas and methane, obtained as disclosed hereinabove, after the preliminary possible separation of any possibly formed formaldehyde, to react, in the presence of catalysts capable of producing methanol and of converting the so produced methanol into dimethyl ether, by operating at a temperature higher than 150 °C and lower than 400 °C and under a pressure higher than 0.1 MPa and lower than 10 MPa.

The integrated process for F-T syntheses from synthesis gas essentially consists in causing the synthesis gas obtained by means of the process as disclosed hereinabove, after the preliminary separation, if so desired, of any possibly formed formaldehyde, to react, by operating, in the presence of a suitable catalyst, at a temperature higher than 200 and lower than 400 °C and under a higher pressure than 1 MPa.

The presence of methane in the reactants mixture is presently allowed only if processes with high conversion rates per pass are used.

The considerable reduction in costs which can be accomplished in the syn gas production process makes it possible advantageous integrated processes for converting natural gas into liquid hydrocarbon and/or oxygen containing products via syn gas containing higher methane levels than 5% by volume, to be defined.

In the accompanying figures 1, 2 and 3 the above mentioned integrated processes are schematically shown.

In Figure 1, the schematic is shown of the integrated process for F-T syntheses from natural gas via syn gas obtained by means of the process according to the present invention.

Natural gas (1) and oxygen (2) are fed to the reactor (3) in which the catalytic partial oxidation of natural gas takes place, with synthesis gas and formaldehyde being obtained.

Formaldehyde (4) can be separated from synthesis gases (5), which are fed to reactor (10) in which the F-T syntheses take place.

The effluent product (11) is sent to a separation unit (12) from which a stream (13) containing hydrocarbons with 2, or more than 2, carbon atoms, and water; and a stream (14), containing methane and hydrocarbons with 2, or less than 2, carbon atoms are obtained, With the latter being recycled to reactor (3).

In Figure 2 the schematic is displayed of the integrated process for the synthesis of methanol or of methanol-dimethyl ether mixtures from natural gas via syn gas.

Natural gas (1) and oxygen (2) are fed to the reactor (3) in which the catalytic partial oxidation of natural gas takes place, with synthesis gas and formaldehyde being obtained.

Formaldehyde (4) can be separated from synthesis gases (5) which are fed to reactor (20) in which the syntheses of methanol or of methanol-dimethyl ether mixtures takes place.

The leaving product (21) is sent to a separation unit (22) from which a stream (23) containing methanol and oxygen-containing products; and a stream (24), containing methane and hydrocarbons with 2, or less than 2, carbon atoms are obtained, with the latter being recycled to reactor (3).

In Figure 3, the schematic is shown of the integrated process for methanol synthesis under high conversions-rate-per pass conditions, from natural gas via syn gas.

Natural gas (1) and oxygen (2) are fed to the reactor (3) in which the catalytic partial oxidation of natural gas takes place, with synthesis gas and formaldehyde being obtained.

Formaldehyde (4) can be separated from synthesis gases (5) which, after being separated in (6) from CO_2 and H_2O (7), are fed to reactor (30) in which the methanol synthesis takes place.

The effluent product (31) is sent to a separation unit (32), from which a stream (33) essentially containing methanol; and a stream (34) containing methane -- which is recycled to reactor (3) -- are obtained.

The cheapness of these processes is favoured by the possibility of separating from the end reaction products, and recycling to CPO unit, any unreacted light (C_1 and C_2) hydrocarbons.

In greater detail, the integrated process for synthesis gas production and use may employ, in CPO unit, mixtures of natural gas and oxygen or enriched air with molar ratios of O_2/CH_4 which may even be lower than 0.5, even in the absence of steam. The CPO process according to the present invention can also use, under UHSV conditions (ultra-high space velocity), $CH_4/O_2/CO_2$ mixtures not containing steam. The process conditions are such that oxygen will b totally converted in the syn gas production unit, whilst meaningful

amounts of methan may remain in the effluent stream from CPO reactors, in particular when the ratio of $O_2:CH_4$ is lower than 0.5.

The CPO reaction products are mainly constituted by mixtures of H_2, CO, and CH_4 with small amounts of H_2O and CO_2, With HCHO being a reaction byproduct. After separating formaldehyde, which can be recycled to the catalytic partial oxidation step, the CO and H_2 containing mixtures are used for synthetizing methanol and/or dimethyl other (DME) and/or hydrocarbons.

In the event when in the effluent streams leaving the syn gas preparation unit, large amounts remain of unreacted methane, the latter remains as an inert substance during the subsequent step of synthesis of hydrocarbons and/or oxygen containing products, is more easily separated from the heavier reaction products and is recycled to the CPO unit.

These results are very difficult to reach under high pressure conditions: on the contrary, it has surprisingly been found that, by means of such processes as disclosed hereinabove, reactions and variations in selectivity rates can be obtained under superatmospheric pressure. If the production of synthesis gas under UHSV conditions is dedicated to methanol synthesis with high values of conversion rate per passage, reaction conditions will be used in which all oxygen is consumed and CO_2 and H_2O present in synthesis gas will be removed before the hydrogenation step.

The results obtained from the experimental tests disclosed in the following examples show that the catalytic system for the CPO reaction can be described by means of equation [12] without water and carbon dioxide being produced as intermediate products by reaction [9] within a wide range of experimental conditions. In this Way, high conversion rates can be obtained under low temperature and high space velocity conditions, because reaction [12] is very fast and is thermodinamically favoured within a wide temperature range (its equilibrium constant is of round 10^{15} within a temperature range of from 25 to 800 °C), whereas rections [10] and [11] are low and thermodinamically unfavoured at lower temperatures than 750 °C. The high yields of synthesis gas which are obtained even at low temperatures when mixtures of CH_4 and O_2 with ratios of $O_2:CH_4 < 0.5$ (by vol/vol) are used, render particularly advantageous the reactions of methanol or methanol-dimethyl ether mixtures production carried out by means of the high conversion-rate-per-pass processes.

Some examples are now supplied in order to better illustrate the invention, it being anyway understood that the invention is not limited to them, or by them.

EXAMPLE 1

The CPO reactions and methanol synthesis at high values of conversion rate per pass from the resulting mixtures of synthesis gas and methane were carried out inside two reactors, at a pressure of 1.5 MPa.

In reactor "A" the CPO reactions were carried out at a temperature of 750 °C and with a GHSV value of 300,000 h^{-1}. The stream of hot gases leaving the first reactor at the temperature of 750 °C is cooled by means of a coil inside which a water stream flows and is sent (after removing small amounts of steam and CO_2 produced during CPO synthesis) to reactor "B" kept at the temperature of 100 °C, in which methanol synthesis takes place.

The mixture of reaction products was analyzed both at first reactor outlet, and at second reactor outlet, in both cases by gas chromatography.

The reactor inside which the CPO reactions are carried out is constituted by a ceramic alumina tube surrounded by a steel cylinder. The alumina tube secures the chemical inertness of the reactor walls and the steel tube constitutes the strong body which enables the experimental tests to be carried out at higher than atmospheric pressures.

The reaction gas, constituted by CH_4 and O_2 ($O_2:CH_4$ = 0.2:0.8 by vol/vol), flows through the catalytic bed (A) containing 0.5 g of an Rh- and Ru-based catalyst, with a contact time of 10^{-2} seconds (GHSV 300,000 h^{-1}).

The noble metals were deposited on a carrier constituted by silica-grafted alpha-alumina. Rh and Ru constitute 0.5% and 1%, respectively, by weight, of the material. The carrier (silica-grafted alumina) was prepared by means of condensation reactions between the reactive groups on alumina surface and tetraethyl silicate (TES), followed by hydrolysis and calcination. The noble metals were deposited by using hydrocarbonaceous solutions of $Rh_4(CO)_{12}$ and $Ru_3(CO)_{12}$, according to such procedures as disclosed in UK Patent No. 2 240 284, UK Publ. No. 2247485, IT-MI92 A 001953, UK Publ. No. 2274284.

The mixture of products obtained from the CPO step enters a slurry reactor "B" for methanol synthesis. The catalytic system in the slurry reactor was prepared by using CuCl and MeONa as precursors, by operating according to the procedures disclosed in EP-375,071. The copper salt and th alkali metal

alkoxide were charged to the reactor under a nitrogen blanketing atmosphere. The solvent Was then added (90 ml of thoroughly dried anisole) in the presence of methanol (40 mmol) . Th molar concentration f alkoxyde was kept at round 2 M, the concentration of copper salt was 0.08 M. During the step of process start-up, the reactor is pressurized and conditioned at 15 atm with a mixture of CO and H_2 (H_2:CO = 2:1 by vol/vol) and the temperature is increased up to 100 °C before the reaction mixture coming from the CPO reactor enters it. In Table 1, the data of composition of the product mixtures in both reaction steps are reported.

The conversion rate of synthesis gas in methanol synthesis step is of 90% and selectivity to methanol is of 98%. The productivity of the system is limited by the methanol synthesis step and therefore resulted to be of 65 g of MeOH / h·litre of reactor volume.

EXAMPLE 2

In this case, the synthesis gas production passage was carried out at 1.5 MPa in the reactor "A" at the temperature of 750 °C. on a monolithic catalyst which contains Rh and Ru. The reactants mixture (GHSV = 300,000 h^{-1}) contained methane and oxygen in a mutual ratio of O_2:CH_4 = 0.29:0.71. The step of hydrogenation of carbon monoxide to yield methanol in the presence of unreacted methane was carried out by causing the reacted stream to flow through the slurry reactor at 1.0 MPa and at a temperature of 85 °C.

The monolithic catalyst was obtained by dipping an enbloc alumina body into an aluminum hydroxide solution. A layer of hydroxide coats the enbloc body and, after drying and calcination, is converted into a porous hydroxide layer. After this treatment, the surface area of the monolithic body resulted to be of 12 m^2/g (this process is referred to in pertinent technical literature as a "wash-coating" process). The monolithic body was soaked in a hydrocarbonaceous solution of $Rh_4(CO)_{12}$ and $Ru_3(CO)_{12}$ (hexane, Rh:Ru:Ir = 0.1:0.5:0.5, by mol/mol) for 2 hours. Under these conditions, reactions of dissociative chemisorption of the clusters take place, yielding to coating the surface of the monolithic body with a monolayer of noble metals, as it was verified by performing the quantitative analysis of the resulting metal contents (0.08% Rh, 0.4% Ru, 0.3% Ir).

The catalyst for the reactions of methanol syntheses was prepared by blending CuCl (6 mmol), CH_3ONa (80 mmol), methyl formate (50 mmol) with 90 ml of anisole. The experiments were carried out according to the same operating procedures as disclosed in above Example 1; the obtained results are reported in Table 2.

The syn gas conversion in methanol synthesis step was of 92% and the selectivity to methanol was of 98%.

EXAMPLE 3

The synthesis gas production reactions were carried out in reactor "A" over a catalytic bed under a pressure of 3.0 MPa, GHSV = 400,000 h^{-1}, outlet T 750 °C, O_2:CH_4 = 0.41 (by vol/vol). The resulting synthesis gas, containing more than 10% of unreacted methane, was used in a second reactor (B) to perform F-T reactions of hydrocarbon synthesis. The pressure inside reactor "B" was kept at 3 MPa, the temperature at 300 °C.

In CPO synthesis a monolithic catalyst was used which was prepared according to the same procedure as disclosed in Example 2. The catalyst for F-T synthesis was prepared by means of successive impregnations up to incipient wetness, of a gamma-alumina (surface area 150 m^2/g). The first impregnation was carried out with an aqueous solution of cobalt nitrate. After drying at 115 °C, the catalyst was submitted to a second impregnation with an aqueous solution of ruthenium nitrate and then was submitted to a second drying procedure. A third impregnation step was carried out with an aqueous solution of potassium carbonate. After a further drying, the catalyst was calcined up to 350 °C. The end catalyst contained 18% cobalt, 2.5% ruthenium, 1% potassium. The catalytic test was preceded by a thermal reduction treatment at 350 °C, during which through reactors "A" and "B" a nitrogen gas stream containing 25% hydrogen was flown. The compositions of the reaction mixtures and of the products from both reaction step are reported in Table 3.

EXAMPLE 4

The same procedures as disclosed in Example 3 were repeated by using the same catalyst for the CPO reactions and, respectively, the same catalyst for F-T synthesis reactions; however, in this case the mixture of methan and oxygen fed to the CPO reactor "A" inlet contained a ratio of O_2:CH_4 = 0.55. The

results obtained are reported in Table 4.

EXAMPLES 5-7

The experiments disclosed in Examples 1, 2 and 4 were repeated by using, as catalyst, in the first CPO reactor, a platinum-rhodium wire mesh, containing 10% by weight of rhodium. Said mesh has similar characteristics as of the wire meshes used in ammonia oxidations into nitric acid and is constituted by metal wires of 0.076 mm of diameter. Inasmuch as rhodium proved to be particularly active for CPO reactions and particularly inert in coal formation reactions, the meshes were modified by depositing on their surface, by electrochemical way, a layer of rhodium metal, from an aqueous solution of rhodium nitrate. The resulting material proved to be active in CPO reactions carried out under UHSV conditions, with selectivities for CO and H_2 higher than 95% under the same reaction conditions as disclosed in Examples 1-4, but with a lower selectivity to formaldehyde. In following Tables 5, 6 and 7, the results are reported which relate to the first reaction step in which the synthesis gas mixtures are obtained.

EXAMPLE 8

In this case, during the first pass of syn gas production, the same catalysts as of Example 2 were used, but with reactants mixtures containing $CH_4:O_2:CO_2$ = 1:0.5:0.5; whereas, during the following step of F-T synthesis, the catalyst disclosed in Example 3 was used. In the CPO step, the following process conditions were used: GHSV = 400,000 h^{-1}, P = 3 MPa, reactor outlet T = 750 °C. In the F-T synthesis reactor, the following reaction conditions were used: GHSV = 1500 h^{-1}, P = 3 MPa, T 300 °C. The results obtained are reported in Table 8.

Table 1

	OPC INLET (Molar fractions)	OPC OUTLET (Molar fractions)	MeOH OUTLET (Molar fractions)
CH_4	0.800	0.250	0.338
O_2	0.200	—	—
H_2	—	0.460	0.067
CO	—	0.240	0.032
HCHO	—	0.050	—
CH_3CH	—	—	0.553
C_2ox+	—	—	0.004
DME	—	—	0.001
MF	—	—	0.007
(DME = dimethyl ether; MF = methyl formate)			

Table 2

	OPC INLET (Molar fractions)	OPC OUTLET (Molar fractions)	MeOH OUTLET (Molar fractions)
CH_4	0.710	0.077	0.190
O_2	0.29	—	—
H_2	—	0.562	0.111
CO	—	0.281	0.054
HCHO	—	0.080	—
CH_3OH	—	—	0.827
C_2ox+	—	—	0.004
DME	—	—	0.002
MF	—	—	0.012

Table 3

	OPC INLET (Molar fractions)	OPC OUTLET (Molar fractions)	F-T OUTLET (Molar fractions)
CH_4	0.710	0.075	0.117
O_2	0.290	–	–
H_2	–	0.570	0.394
CO	–	0.285	0.224
HCHO	–	0.070	–
CO_2	–	–	–
H_2O	–	–	0.207
C_2 +	–	–	0.058

Table 4

	OPC INLET (Molar fractions)	OPC OUTLET (Molar fractions)	F-T OUTLET (Molar fractions)
CH_4	0.868	0.015	0.013
O_2	0.334	–	–
H_2	–	0.590	0.394
CO	–	0.290	0.224
HCHO	–	0.080	–
CO_2	–	0.010	0.008
H_2O	–	0.015	0.215
C_2 +	–	–	0.058

Table 5

	OPC INLET (Molar fractions)	OPC OUTLET (Molar fractions)
CH_4	0.600	0.250
O_2	0.200	–
H_2	–	0.240
CO	–	0.480
HCHO	–	0.030
CO_2	–	–
H_2O	–	–

Table 6

	OPC INLET (Molar fractions)	OPC OUTLET (Molar fractions)
CH_4	0.710	0.075
O_2	0.280	–
H_2	–	0.295
CO	–	0.590
HCHO	–	0.040
CO_2	–	–
H_2O	–	–

Table 7

	OPC INLET (Molar fractions)	OPC OUTLET (Molar fractions)
CH_4	0.666	0.001
O_2	0.334	–
H_2	–	0.300
CO	–	0.600
HCHO	–	0.080
CO_2	–	0.009
H_2O	–	0.010

Table 8

	OPC INLET (Molar fractions)	OPC OUTLET (Molar fractions)	F-T OUTLET (Molar fractions)
CH_4	0.500	0.031	0.109
O_2	0.250	–	–
H_2	–	0.485	0.106
CO	–	0.303	0.160
HCHO	–	0.030	–
CO_2	0.250	0.106	0.187
H_2O	–	0.045	0.374
C_2 +	–	–	0.064

Claims

1. Process of catalytic partial oxidation of natural gas in order to obtain synthesis gas and formaldheyde, characterized in that such an oxidation is carried out by means of a catalyst constituted by one or more compounds of metals from Platinum Group, which is given the shape of a wire mesh, or is deposited on a carrier made from inorganic compounds, in such a way that the level of metal or metals from Platinum Group, by weight, is comprised within the range of from 0.1 to 20% of the total weight of catalyst and carrier, by operating at temperatures comprised within the range of from 300 to 950°C, under pressures comprised within the range of from 0.5 to 50 atm, at space velocities comprised within the range of from 20.000 to 1.500.000 h^{-1}.

2. Process according to claim 1, in which the temperatures are comprised within the range of from 500 to 850°C, the pressures within the range of from 1 to 40 atm and the space velocities within the range of from 100.000 to 608.000 h^{-1}.

3. Process according to claim 1, in which the percent by weight of metal or metals from Platinum Group is comprised within the range of from 0.1 to 5% by weight, based on total catalyst and carrier weight.

4. Process according to claim 1, in which the metals from Platinum Group are selected from rhodium, ruthenium and iridium.

5. Process according to one of claims from 1 to 4 in which the molar ratio of O_2:CH_4 is lower than 0.5.

6. Process for the synthesis of methanol from synthesis gas, consisting in causing the synthesis gas obtained by means of the process according to one of claims from 1 to 5, after the preliminary possible separation of formed formaldehyde, to react, by means f a suitable catalyst, by operating in the case of th high-conversion-per-pass syntheses, after additionally separating CO_2 and H_2O from said synthesis gas, at a temperature which is higher than 40°C and lower than 200°C and under a higher pressure than 1 MPa; and, in the case of the syntheses by the conventional route, at a temperature high r than 200°C and lower than 350°C, and under a higher pressure than 1 MPa.

7. Process for Fischer-Tropsch (F-T) syntheses from synthesis gas, consisting in causing the synthesis gas obtained by means of the process according to one of claims from 1 to 5, after the preliminary possible separation of formed formaldehyde, to react, by means of a suitable catalyst, by operating at a temperature higher than 200 and lower than 400 °C and under a higher pressure than 1 MPa.

8. Process for the synthesis of methanol-dimethyl ether mixtures from synthesis gas, consisting in causing the mixture of synthesis gas and methane, obtained by means of the process as claimed in one of claims from 1 to 5 , after the preliminary possible separation of formed formaldehyde, to react, in the presence of catalysts capable of producing methanol and of converting the so produced methanol into dimethyl ether, by operating at a temperature higher than 150 °C and lower than 400 °C and under a pressure higher than 0.1 MPa and lower than 10 MPa.

Fig.1

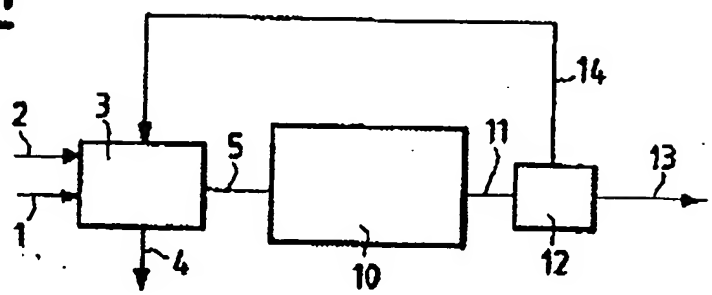


Fig.2

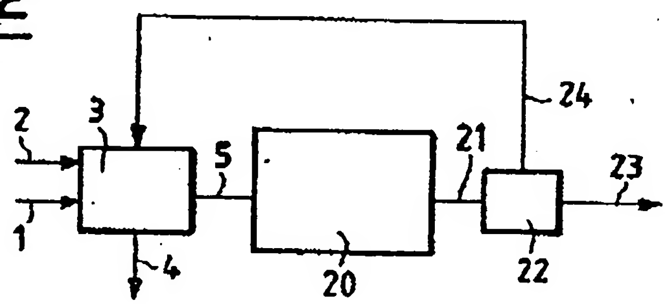
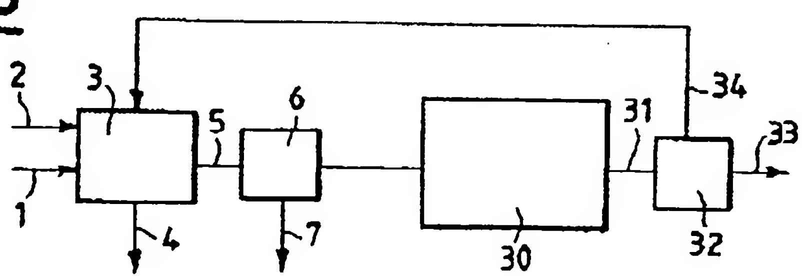


Fig.3



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EUROPEAN SEARCH REPORT

Application Number
EP 94 20 2270

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	CATALYSIS LETTERS, vol.6, 1990, BASEL CH pages 181 - 186 P.D.F.VERNON ET AL. 'partial oxidation of methane to synthesis gas' * the whole document *	1-8	C01B3/38 C01B3/40 C07C1/04 C07C29/151 C07C31/04
X	GB-A-2 239 406 (GAS RESEARCH INSTITUTE) * page 1, line 19 - line 30 * * page 3, line 30 - page 5, line 7 * * page 7, line 9 - page 8, line 12 *	1-5	
X	EP-A-0 303 438 (DAVY MCKEE CORPORATION) * column 2, line 50 - column 4, line 2 * * column 6, line 46 - column 7, line 45 * * example * * claims 1-5,10-14 *	1,2,4,5	
X	APPLIED CATALYSIS B: ENVIRONMENTAL, vol.1, no.2, 26 June 1992, AMSTERDAM, NL pages 89 - 100 J.K. HOCHMUTH 'Catalytic partial oxidation of methane over a monolith supported catalyst' * the whole document *	1-3,5	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C01B C07C
A	W. GERHARTZ, Y.S. YAMAMOTO (EDS.) 'Ullmann's Encyclopedia of Industrial Chemistry, Vol. A5, Carbon Monoxide' 1986 , VCH * 9.2 Production of Organic Chemicals *	6-8	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28 November 1994	Van der Poel, W

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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